



---

**(HBCU) Photo-switchable Donor-Acceptor for Organic Photovoltaic Cells**

**Luis Echegoyen  
UNIVERSITY OF TEXAS AT EL PASO**

---

**11/05/2015  
Final Report**

**DISTRIBUTION A: Distribution approved for public release.**

**Air Force Research Laboratory  
AF Office Of Scientific Research (AFOSR)/ RTB2  
Arlington, Virginia 22203  
Air Force Materiel Command**

<b>REPORT DOCUMENTATION PAGE</b>					Form Approved OMB No. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services, Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.</p>						
<b>1. REPORT DATE (DD-MM-YYYY)</b> 01-12-2015		<b>2. REPORT TYPE</b> Final Performance		<b>3. DATES COVERED (From - To)</b> 01-03-2012 to 31-08-2015		
<b>4. TITLE AND SUBTITLE</b> Photo-switchable Donor-Acceptor (D-A) Dyad Interfacial Self-Assembled Monolayers for Organic Photovoltaic Cells				<b>5a. CONTRACT NUMBER</b>		
				<b>5b. GRANT NUMBER</b> FA9550-12-1-0053		
				<b>5c. PROGRAM ELEMENT NUMBER</b> 61102F		
<b>6. AUTHOR(S)</b> Luis Echegoyen				<b>5d. PROJECT NUMBER</b>		
				<b>5e. TASK NUMBER</b>		
				<b>5f. WORK UNIT NUMBER</b>		
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> UNIVERSITY OF TEXAS AT EL PASO 500 UNIV ST ADMIN BLDG 209 EL PASO, TX 79968-0001 US				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>		
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b> AFRL/AFOSR RTB2		
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b>		
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> A DISTRIBUTION UNLIMITED: PB Public Release						
<b>13. SUPPLEMENTARY NOTES</b>						
<b>14. ABSTRACT</b> Several Donor-Acceptor (D-A) dyads were designed and prepared to be used as photoswitched interfacial layers to polarize organic solar cells when irradiated to increase the photoconversion efficiencies. Some D-A dyads were designed to be anchored on TiO <sub>2</sub> supports to function as Dye Sensitized Solar Cells (DSSCs). The concept of photoswitched interfacial polarization was clearly demonstrated using impedance spectroscopy for several triphenylamine-fullerene dyads, but their performance in photovoltaic devices was not remarkable, likely due to the presence of pinholes in the self-assembled monolayers. Some of the new compounds performed relatively well in DSSCs, some attaining PCEs of 4.7-5.6%.						
<b>15. SUBJECT TERMS</b> organic, solar cell, photo-switchable						
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>  UU	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b> Luis Echegoyen	
<b>a. REPORT</b>  Unclassified	<b>b. ABSTRACT</b>  Unclassified	<b>c. THIS PAGE</b>  Unclassified			<b>19b. TELEPHONE NUMBER (Include area code)</b> 915-747-7573	

1.

**1. Report Type**

Final Report

**Primary Contact E-mail**

Contact email if there is a problem with the report.

echegoyen@utep.edu

**Primary Contact Phone Number**

Contact phone number if there is a problem with the report

915-747-7573

**Organization / Institution name**

Univ. of Texas - El Paso

**Grant/Contract Title**

The full title of the funded effort.

(HBCU) Photo-switchable Donor-Acceptor Dyads for Organic Photovoltaics

**Grant/Contract Number**

AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-12-1-0053

**Principal Investigator Name**

The full name of the principal investigator on the grant or contract.

Luis Echegoyen

**Program Manager**

The AFOSR Program Manager currently assigned to the award

Charles Lee

**Reporting Period Start Date**

03/01/2012

**Reporting Period End Date**

08/31/2015

**Abstract**

Several Donor-Acceptor (D-A) dyads were designed and prepared to be used as photoswitched interfacial layers to polarize organic solar cells when irradiated to increase the photoconversion efficiencies. Some D-A dyads were designed to be anchored on TiO<sub>2</sub> supports to function as Dye Sensitized Solar Cells (DSSCs). The concept of photoswitched interfacial polarization was clearly demonstrated using impedance spectroscopy for several triphenylamine-fullerene dyads, but their performance in photovoltaic devices was not remarkable, likely due to the presence of pinholes in the self-assembled monolayers. Some of the new compounds performed relatively well in DSSCs, some attaining PCEs of 4.7-5.6%.

**Distribution Statement**

This is block 12 on the SF298 form.

Distribution A - Approved for Public Release

**Explanation for Distribution Statement**

If this is not approved for public release, please provide a short explanation. E.g., contains proprietary information.

**SF298 Form**Please attach your [SF298](#) form. A blank SF298 can be found [here](#). Please do not password protect or secure the PDF

The maximum file size for an SF298 is 50MB.

**Upload the Report Document. File must be a PDF. Please do not password protect or secure the PDF . The maximum file size for the Report Document is 50MB.**

[Report Document.pdf](#)

**Upload a Report Document, if any. The maximum file size for the Report Document is 50MB.**

**Archival Publications (published) during reporting period:**

1. Alexis Tigreros, Vivek Dhas, Alejandro Ortiz, Braulio Insuasty, Nazario Martín and Luis Echegoyen, "Influence of acetylene-linked  $\pi$  -spacers on triphenylamine-fluorene dye sensitized solar cells performance," Solar Energy Mater. and Solar Cells, 121, 61-68, 2014 (DOI: 10.1016/j.solmat.2013.10.035).
2. Mahsa Hosseini, Danisha M. Rivera-Nazario, Ping Peng, and Luis Echegoyen, "Self-Assembled Monolayers of C60-Triphenylamine Dyads as Photo-Switched Interfacial Layers for Potential Application in Photovoltaic Cells," ACS Applied Materials & Interfaces, 6, 3712-3720, 2014 (DOI: 10.1021/am500049q).
3. Carlos Alberto Echeverry, Alberto Insuasty, María Ángeles Herranz, Alejandro Ortiz, Robert Cotta, Vivek Dhas, Luis Echegoyen, Braulio Insuasty, Nazario Martín, "Organic dyes containing 2-(1,1-dicyanomethylene)rhodanine as an efficient electron acceptor and anchoring unit for Dye-Sensitized Solar Cells," Dyes and Pigments, 107, 9-14, 2014 (DOI: 10.1016/j.dyepig.2014.03.010).
4. Danny Arteaga, Robert Cotta, Alejandro Ortiz, Braulio Insuasty, Nazario Martín, and Luis Echegoyen, "Zn(II)-porphyrin dyes with several electron acceptor groups linked by vinyl-fluorene or vinyl-thiophene spacers for dye-sensitized solar cells," Dyes and Pigments, 112, 127-137, 2014 (DOI: 10.1016/j.dyepig.2014.06.028).
5. Agustín Molina-Ontoria, Danisha M. Rivera-Nazario, Alexis Tigreros, Alejandro Ortiz, José E. Nuñez, Braulio Insuasty, Daniela Lueders, Silke Wolfrum, Dirk M. Guldi and Luis Echegoyen, "Geometric Influence on Intramolecular Photoinduced Electron Transfer in Platinum(II) Acetylide-linked Donor-Acceptor Assemblies," Chem. Eur. J., 20, 11111-11119, 2014 (DOI: 10.1002/chem.201402616).
6. Agustín Molina-Ontoria, María Gallego, Luis Echegoyen, Emilio M. Pérez and Nazario Martín, "Organic solar cells based on bowl-shaped small molecules," RSC Advances, 5, 31541-31545, 2015 (DOI: 10.1039/c5ra02073e).
7. Alexis Tigreros, Danisha M. Rivera-Nazario, Alejandro Ortiz, Nazario Martín, Braulio Insuasty and Luis A Echegoyen, "Fluore-9-ylidene based dyes for dye-sensitized solar cells," Eur. J. Org. Chem., 25, 5537-5545, 2015 (DOI: 10.1002/ejoc.201500602).

**Changes in research objectives (if any):**

The main original aim of this project was to design and prepare a series of Donor-Acceptor (D-A) dyads that could be used as photoswitched self-assembled monolayers (SAMs) to polarize bulk heterojunction (BHJ) solar cells to increase their efficiency. While the photoswitched mechanism was clearly demonstrated (see article #2 above) the resulting SAMs resulted in relatively low photoconversion efficiencies when incorporated in BHJ solar cells, likely because of pinholes leading to shorts. However, several of the designed D-A dyads were modified to be incorporated into Dye Sensitized Solar Cells (DSSCs) and these performed fairly well (see articles # 1, 3, 4 and 7), with some exhibiting PCEs of 5.6% and 4.7%.

**Change in AFOSR Program Manager, if any:**

**Extensions granted or milestones slipped, if any:**

A six month extension was granted, from February to August, 2015.

**AFOSR LRIR Number**

**LRIR Title**

**Reporting Period**

**Laboratory Task Manager**

**Program Officer**

**Research Objectives**

## Technical Summary

### Funding Summary by Cost Category (by FY, \$K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

## Report Document

### Report Document - Text Analysis

### Report Document - Text Analysis

## Appendix Documents

## 2. Thank You

## E-mail user

Nov 05, 2015 14:23:06 Success: Email Sent to: echegoyen@utep.edu

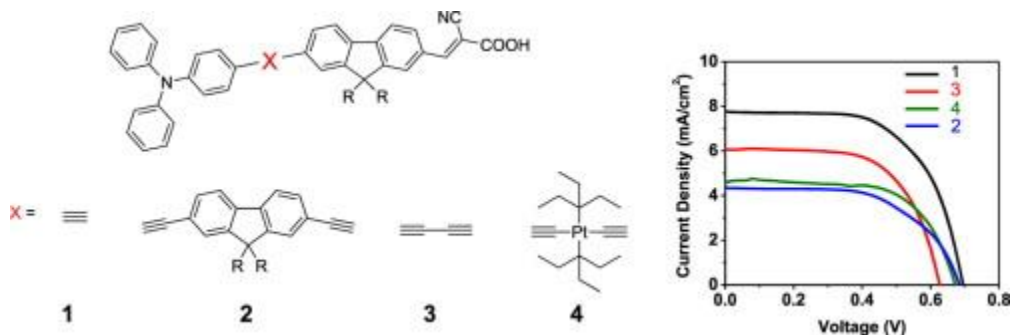
## Final Report for Grant FA9550-12-1-0053

### Period Covered – 1 March, 2012 – 31 August, 2015

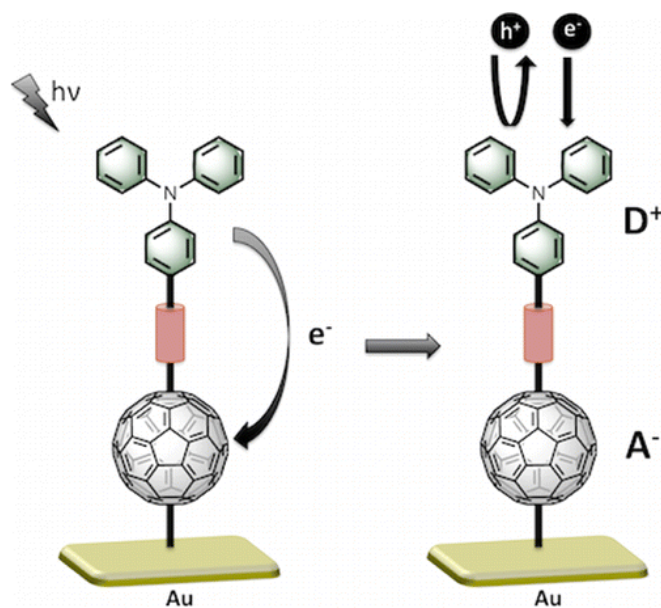
Since this grant resulted in seven acknowledged publications and since the corresponding references and graphical abstracts are very descriptive of the work performed and clearly define the salient features of the work, we have compiled these graphical abstracts to form the final report for the grant.

1. Alexis Tigreros, Vivek Dhas, Alejandro Ortiz, Braulio Insuasty, Nazario Martín and Luis Echegoyen, "Influence of acetylene-linked  $\pi$ -spacers on triphenylamine-fluorene dye sensitized solar cells performance," *Solar Energy Mater. and Solar Cells*, 121, 61-68, **2014** (DOI: 10.1016/j.solmat.2013.10.035).

Four new organic dyes, **1–4**, containing triphenylamine (TPA) donors connected through different acetylene linkages to fluorene bridges and cyanoacrylic acid acceptors were designed and synthesized for photoconversion in dye sensitized solar cells (DSSCs). Their absorption spectra, electrochemical and photovoltaic properties were investigated. Shortening the bridge between the TPA moiety and the anchoring group leads to a dramatic increase in the overall photoconversion efficiency (**1**>**3**>**4**>**2**).



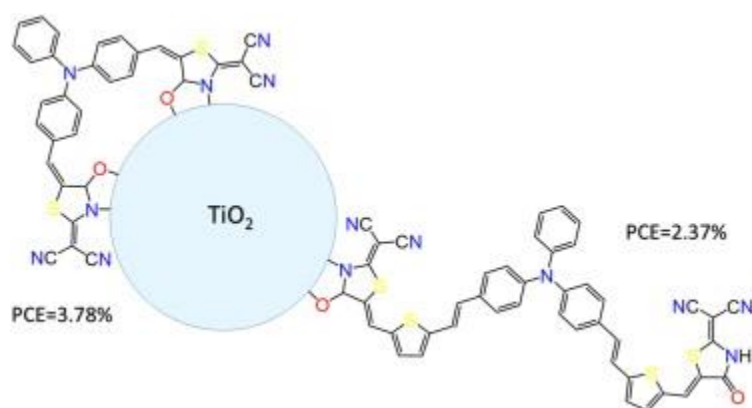
2. Mahsa Hosseini, Danisha M. Rivera-Nazario, Ping Peng, and Luis Echegoyen, "Self-Assembled Monolayers of C<sub>60</sub>-Triphenylamine Dyads as Photo-Switched Interfacial Layers for Potential Application in Photovoltaic Cells," *ACS Applied Materials & Interfaces*, 6, 3712-3720, **2014** (DOI: 10.1021/am500049q).



C<sub>60</sub>-Triphenylamine dyads were synthesized for incorporation as photoswitched interfacial layers in organic photovoltaic (OPV) cells. Self-assembled monolayers (SAMs) of these dyads on gold (through S–Au and C<sub>60</sub>–Au interactions) were prepared through one or two adsorption processes, and their packing densities were fully characterized. Analysis using quartz crystal microbalance

(QCM) and electrochemical impedance spectroscopy (EIS) measurements indicated that all SAMs exhibit dense coverage on the gold surfaces. Electrochemical desorption in KOH confirmed that the *cis*-1 dyad is anchored to the gold surface through its thiol group. Impedance measurements in the absence and presence of UV irradiation were performed to observe the photoswitched properties of these surface confined dyads. Upon UV light exposure of the SAMs, the charge-transfer resistance decreased when  $\text{Fe}(\text{CN})_6^{3-/4-}$  was used as the probe redox couple and increased with  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ , confirming the generation of positive charges on the surface upon UV irradiation.

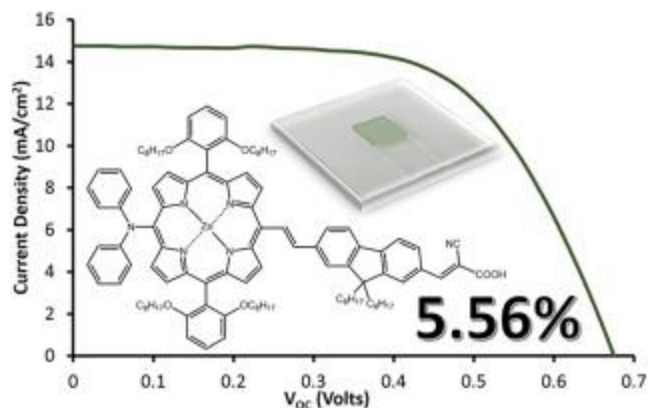
3. Carlos Alberto Echeverry, Alberto Insuasty, María Ángeles Herranz, Alejandro Ortíz, Robert Cotta, Vivek Dhas, Luis Echegoyen, Braulio Insuasty, Nazario Martín, "Organic dyes containing 2-(1,1-dicyanomethylene)rhodanine as an efficient electron acceptor and anchoring unit for Dye-Sensitized Solar Cells," *Dyes and Pigments*, 107, 9-14, **2014** (DOI: 10.1016/j.dyepig.2014.03.010).



Here we report the synthesis and characterization of five new organic dyes based on 2-(1,1-dicyanomethylene)rhodanine, which simultaneously serves as an efficient electron-acceptor moiety and anchoring unit to the  $\text{TiO}_2$ . Triphenylamine was used as the electron donor and a vinylthiophene unit was introduced to increase the pi-conjugation of the system and to

widen the absorption region. The dye containing two 2-(1,1-dicyanomethylene)rhodanine units and no thiophene units showed the best photovoltaic performance with a short-circuit photocurrent density of  $7.76 \text{ mA/cm}^2$ , an open circuit photovoltage of  $0.62 \text{ V}$ , and a fill factor of  $0.68$ , corresponding to an overall conversion efficiency of  $3.78\%$  under AM 1.5 irradiation ( $100 \text{ mW/cm}^2$ ).

4. Danny Arteaga, Robert Cotta, Alejandro Ortiza, Braulio Insuasty, Nazario Martin, and Luis Echegoyen, "Zn(II)-porphyrin dyes with several electron acceptor groups linked by vinyl-fluorene or vinyl-thiophene spacers for dye-sensitized solar cells," *Dyes and Pigments*, 112, 127-137, **2014** (DOI: 10.1016/j.dyepig.2014.06.028).



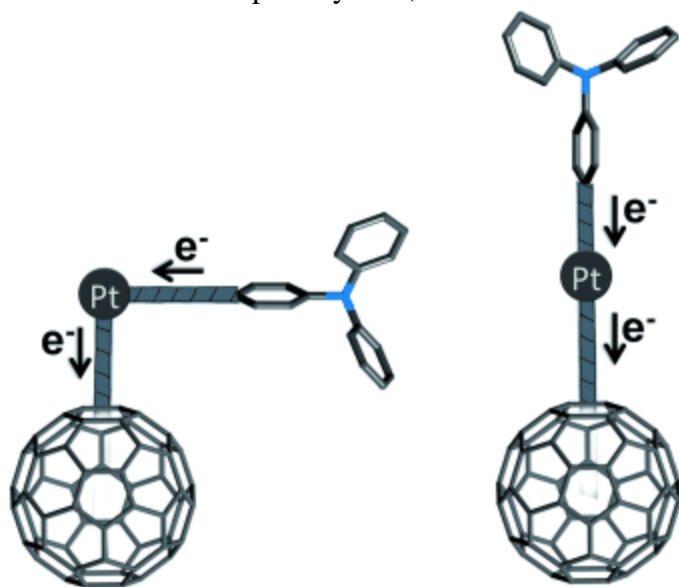
Herein we report the design, synthesis, and characterization of a series of new organic dyes, as well as their application in dye-sensitized nanocrystalline  $\text{TiO}_2$  solar cells. In the designed dyes, the diphenylamine Zn(II) porphyrin group plays the role of



the core electron donor unit and the cyanoacrylic acid, rhodanine acetic acid, and dicyanorhodanine groups are the acceptors. These electroactive units are linked by either vinyl-fluorene or vinyl-thiophene spacer units. To study the electron distribution and the intramolecular charge transfer the HOMO-LUMO levels of the dyes were calculated by computational methods and experimentally using electrochemical measurements. The DSSCs based on the dyes bearing a cyanoacrylic acid acceptor group showed the best photovoltaic performance with short-circuit photocurrent densities of 12.66 and 13.58 mA/cm<sup>2</sup>, open-circuit photovoltages of 0.675 and 0.651 V, and fill factors of 0.628 and 0.441, corresponding to an overall conversion efficiency of 5.56 and 4.13%, respectively, under AM 1.5 irradiation (100 mW/cm<sup>2</sup>).

5. Agustín Molina-Ontoria, Danisha M. Rivera-Nazario, Alexis Tigreros, Alejandro Ortiz, José E. Nuñez, Braulio Insuasty, Daniela Lueders, Silke Wolfrum, Dirk M. Guldi and Luis Echegoyen, "Geometric Influence on Intramolecular Photoinduced Electron Transfer in Platinum(II) Acetylide-linked Donor-Acceptor Assemblies," *Chem. Eur. J.*, **20**, 11111-11119, **2014** (DOI: 10.1002/chem.201402616).

A new donor-acceptor system, in which the electron donor triphenylamine (TPA) and the



electron acceptor C<sub>60</sub> are bridged through a *cis*- or *trans*-platinum(II) acetylide spacer have been prepared. Ground-state studies were conducted using electrochemistry and UV/Vis spectroscopy. Fluorescence studies suggested that charge transfer is the deactivation mechanism for the singlet excited state, and this was verified by transient absorption spectroscopy. Selective photoexcitation of **1** and **2** at 387 nm leads to a fast charge transfer between the TPA and C<sub>60</sub>, which gives rise to a radical ion-pair state (TPA<sup>•+</sup>-Pt-C<sub>60</sub><sup>•-</sup>). Our results suggest that charge transfer is favored for the *cis*

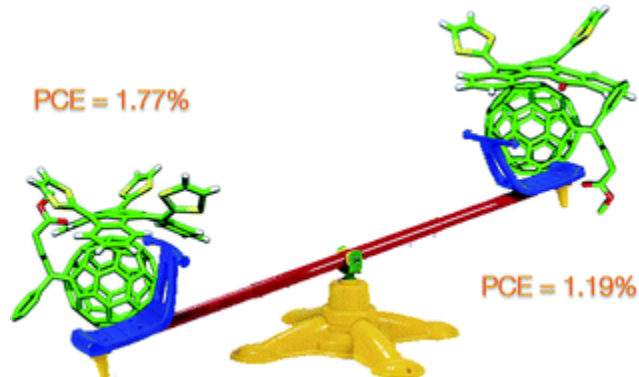
configuration while the presence of the *trans* configuration in the Pt<sup>II</sup> diacetylide results in a longer-lived charge separated states.

6. Agustín Molina-Ontoria, María Gallego, Luís Echegoyen, Emilio M. Pérez and Nazario Martín, "Organic solar cells based on bowl-shaped small molecules," *RSC Advances*, **5**, 31541-31545, **2015** (DOI: 10.1039/c5ra02073e).

The light absorption ability and morphology of the active components are two of the key factors that determine the energy conversion efficiency in organic solar cells (OSCs). Determining the relative importance of each of these aspects is decisive for the construction of more efficient OSCs. Here we introduce two  $\pi$ -extended derivatives of tetrathiafulvalene as electron donors for solution-processed small-molecule bulk-heterojunction solar cells. Both of them exhibit similar



bowl-shaped geometry, excellent electron-donor characteristics and relatively large association constants with fullerenes in solution (on the order of  $10^4 \text{ M}^{-1}$  for truxTTF and  $10^3 \text{ M}^{-1}$  for truxTTF-CO in several solvents at room temperature). The substitution of one dithiole ring in truxTTF-CO for a carbonyl results in an intramolecular push-pull effect, which enhances its light-harvesting properties, with the onset of absorbance reaching 650 nm. The introduction of a third dithiole ring, results in a more pronounced concave shape in truxTTF, allowing a better self-assembly with fullerenes which in turn leads to a more favourable morphology. However, the light-absorption ability of truxTTF is limited to *ca.* 500 nm. We prepared bulk-heterojunction solar cells using phenyl- $\text{C}_{60}$ -butyric acid methyl ester ( $\text{PC}_{61}\text{BM}$ ) and  $\text{PC}_{71}\text{BM}$  as electron-acceptors and bowl-shaped truxTTF and truxTTF-CO as electron-donors. The devices prepared utilizing truxTTF performed significantly better (PCE up to 1.77% with  $\text{PC}_{71}\text{BM}$  and 0.92% with  $\text{PC}_{61}\text{BM}$ ) than the truxTTF-CO counterpart (PCE up to 1.19% with  $\text{PC}_{71}\text{BM}$  and 0.56% with  $\text{PC}_{61}\text{BM}$ ).



7. Alexis Tigreros, Danisha M. Rivera-Nazario, Alejandro Ortiz, Nazario Martin, Braulio Insuasty and Luis A Echegoyen, "Fluore-9-ylidene based dyes for dye-sensitized solar cells," *Eur. J. Org. Chem.*, 25, 5537-5545, **2015** (DOI: 10.1002/ejoc.201500602).

Three new dyes (1–3) with a triarylamine electron donor, a cyanoacrylic acid moiety as both electron acceptor and anchoring group, and a fluorene-9-ylidene moiety as an antenna were synthesized, and their electrochemical, photophysical, and photovoltaic properties were evaluated. Despite minor differences in absorption properties, as the starburst shape of the dyes increases and highly hindered hydrophobic groups are introduced, the measured open-cell voltage ( $V_{oc}$ ) increased noticeably from 0.79 to 0.83 V, and the power-conversion efficiency (PCE) value increased from 3.98 to 4.73 %.

